

Soft Microelectrode Linear Array For Scanning Electrochemical Microscopy

-- Electronic Supporting Information --

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SI-1: Sample holder for the soft stylus microelectrode array

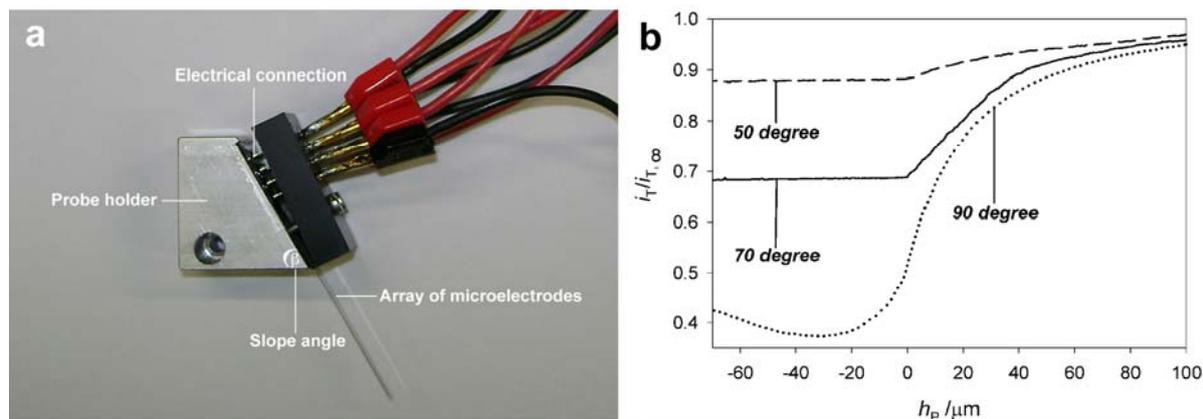


Figure SI-1. a) Photograph of the holder for the array probe with a predefined tilt. b) Approach curves over an insulating substrate in 2.1 mM FcCH₂OH, 0.1 M KNO₃. $E_T = 0.3$ V Vs QRE, translation rate 0.5 $\mu\text{m/s}$. The different angles represent the angle between the sample surface and the probe defined as slope angle β in (a).

Figure SI-1a shows the SECM holder developed for inclining the probe by a certain angle with the aim of presetting the probe tilting degree and direction when scanning in contact regime. As can be seen in the approach curves in Figure SI-1b the contrast increases as the angle of probe axis and sample approaches 90°. However, inclined samples provide a constant current after mechanically touching the surface.

SI-2 Integrity of the Parylene Coating of Soft Stylus Microelectrode Arrays

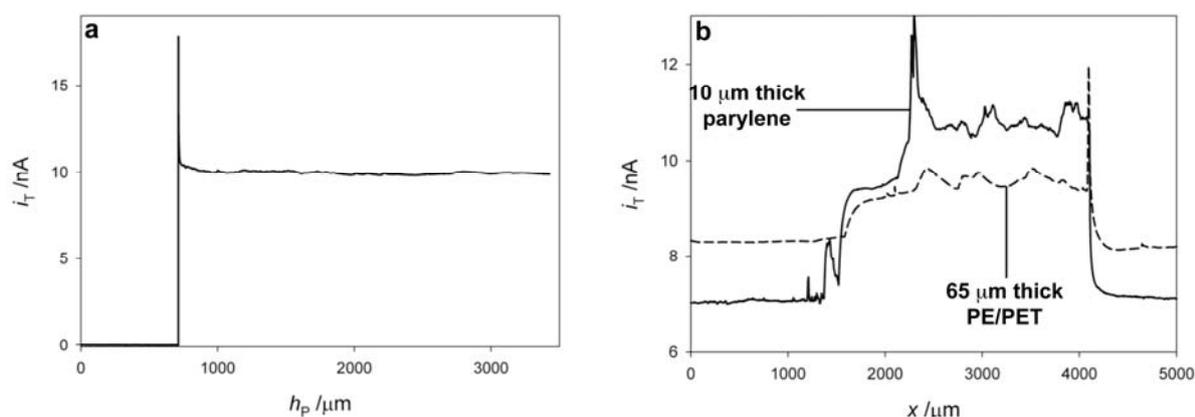


Figure SI-2. a) Experimental approach curve with a parylene coated soft stylus probe toward a solution of FcCH_2OH 2.1 mM in KNO_3 0.1 M. b) Lateral SECM line scan with a soft stylus probe coated by a 10 μm thick parylene coating (continuous line) and a 65 μm thick polyethylene/polyethylene terephthalate lamination foil (dashed line). $E_T = 0.3$ V, step size = 5 μm , $v_T = 10 \mu\text{m/s}$. 2.1 mM FcCH_2OH .

Figure SI-2a shows the approach curve of the microelectrode array from air toward the air/solution interface. Upon contact the current rises. After decay of the capacitive current the current settles on a constant value coming from the electrolysis of 2.1 mM of FcCH_2OH contained in the electrolyte. The current does not rise as the probe is further immersed into the electrolyte. This proves the good sealing of the carbon track by the parylene coating since pinholes or defects in this coating would lead to currents that would increase with continuous immersion.

Figure SI-2b shows a line scans in contact mode over a thick carbon electrode (118 μm thick) measured with two soft stylus probes with different thickness of the insulating cover of the carbon tracks. A higher current contrast is obtained when using parylene coating for closing the carbon tracks because the thinner coating decreases the effective working distance.

SI-3: Working distance of the *unbent* and *bent* soft array of microelectrodes

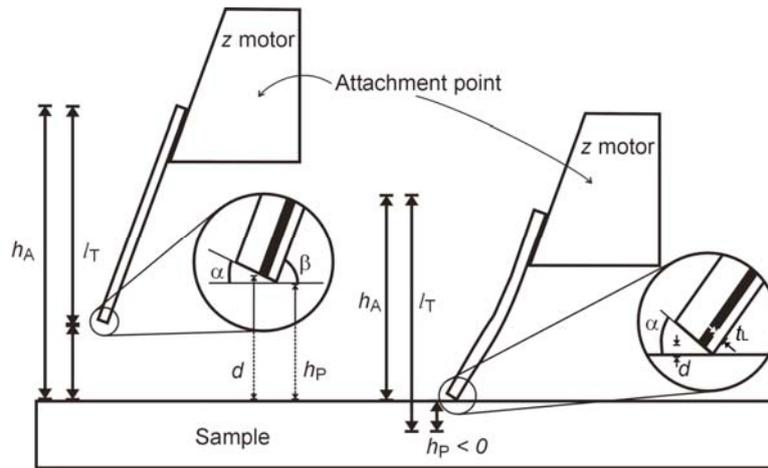


Figure SI-3. Schematic representation of the SECM contact mode and the working distance for unbent and bent soft array of microelectrodes.

In order to plot the approach curves after touching of the sample, a new vertical coordinate h_p was defined. It is the vertical difference $h_p = h_A - l_T$ between the height of the attachment point above the sample h_A and the vertical extension l_T of the unbent probe. Thus the effective working distance d is completely defined by

$$d = \begin{cases} d = h_p + t_L \sin(\alpha); & (h_p \geq 0, \text{ non-contact regime}) \\ d = t_L \sin(\alpha); & (h_p < 0, \text{ contact regime}) \end{cases} \quad (\text{SI-3-1})$$

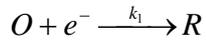
where α angle between the cross sectional plane of the probe and the sample surface and t_L is the thickness of the polymer film covering the carbon tracks. The situation is shown in Figure SI-3.

SI-4: Details of the Finite Element Method (FEM) Simulations

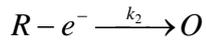
The model under investigation can be described by the diffusion equations for redox active species assuming steady-state conditions

$$\nabla(-D_i \nabla c_i) = 0 \quad (\text{SI-4-1})$$

where D_i and c_i are the diffusion coefficient and concentration of species i , respectively. The electrochemical response of the electrode can be depicted as the consequence of the following reaction at the probe



and at the substrate



where k_1 and k_2 represents the heterogeneous rate constants for the forward and backward reaction, respectively. The reaction rates can be defined by

$$v_{probe} = k_1 * c_o \quad (\text{SI-4-2})$$

$$v_{sub} = k_2 * (c_{bulk} - c_o) \quad (\text{SI-4-3})$$

v_{probe} and v_{sub} indicate the reaction rates at the electrode and at the substrate, while c_o and c_{bulk} are the local and bulk concentrations of species O. In this work we assume steady state conditions with $k_1 = k_2 = 10^6 \text{ m s}^{-1}$. The diffusion coefficients for species O and R were set to $6.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which corresponds to diffusion coefficient of ferrocene methanol in water and c_{bulk} of O species was 2 mM. By applying the appropriate boundary conditions, the solution of the differential equations is the local concentration c_o . The probe current can be calculated by integrating the normal diffusive fluxes of species O at the electrode surface.

The body of array was simulated as a parallelepiped with dimensions $125\ \mu\text{m} \times 2000\ \mu\text{m} \times 1000\ \mu\text{m}$ which is placed in a box of $2000\ \mu\text{m} \times 3000\ \mu\text{m} \times 1000\ \mu\text{m}$. The bottom of the array was placed at least $1000\ \mu\text{m}$ far away from the top and side planes of the box. The assumed electrode geometry of the soft microelectrode array is shown in Figure 3a. The active area of all the microelectrodes was approximated to a quarter-moon shaped (i.e. $20\ \mu\text{m}$ depth and $40\ \mu\text{m}$ width).

The total mesh employed in the present work for simulating an array of three microelectrodes is shown in Figure S4-1. The minimal mesh size was set to $0.8\ \mu\text{m}$ at the edges of active surface area and the edges of the array.

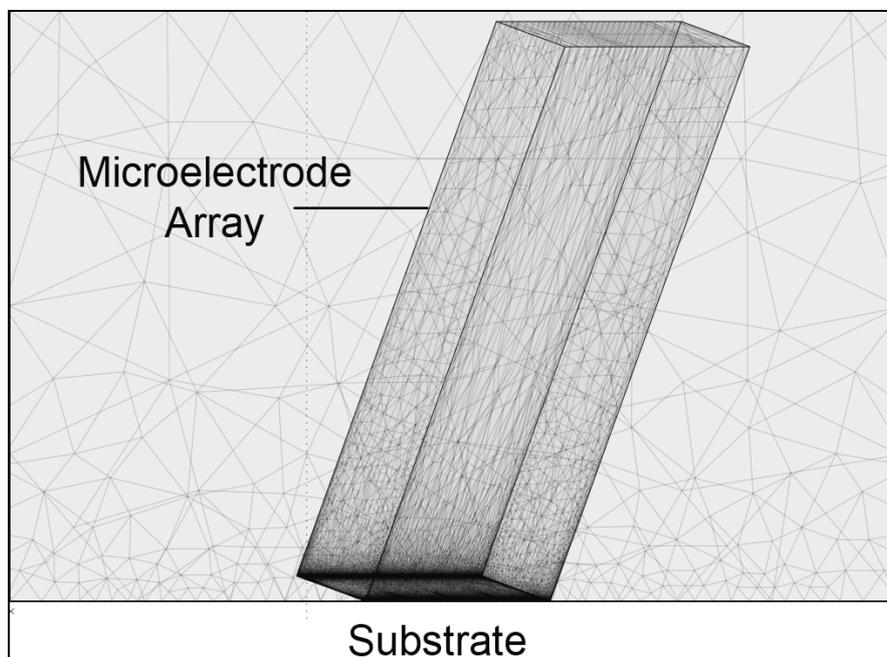


Figure S4-1. Used mesh for representing the total simulated system (i.e. soft microelectrode array and conducting or insulating substrate)

The microelectrode array was approached to the substrate presenting a take-off angle α equal to 70 degree. $130\ \mu\text{m}$ and $500\ \mu\text{m}$ electrode-to-electrode distances were employed for assessing the effect of the diffusion layer overlapping on the SECM approach curves. The approach curves started at a probe-substrate distance of $h_p = 100\ \mu\text{m}$ and 20 further points were calculated until touching the substrate.